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BALLOONBORNE MEASUREMENTS OF POLAR STRATOSPHERIC CLOUDS AND OZONE AT -93° C IN THE ARCTIC IN FEBRUARY 1990

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Abstract. Balloonborne measurements of ozone and particle size distributions at Kiruna, Sweden indicate that on 6 February 1990 a major cooling event occurred over northern Scandinavia, reaching temperatures as low as -93° C at 22 km. Both nitric acid trihydrate and water ice clouds formed in the 19 to 23 km region. The temperature of the appearance of the water ice clouds is consistent with about 5 ppmv of water vapor at 22 km. The particle size distributions suggest that a sizeable degree of denitrification had occurred in the 19 to 23 km region in this air mass. Although ozone levels may have been reduced by a small degree of chemical depletion, the ozone "minihole" of 165 DU observed by TOMS was probably an artifact caused by ice clouds at 22 km since two ozonesonde measurements on that day indicated total ozone values of about 285 DU.

Introduction

Balloonborne optical particle counters and digital electrochemical ozonesondes were used in this study. The particle counter measures light scattered in the forward direction by individual particles as they pass through the instrument at a sampling rate of about 10 liters per minute. Originally designed for studying the stratospheric sulfate layer, the counter has seen several modifications in order to provide polar stratospheric cloud (PSC) measurements in which larger, less concentrated, more volatile nitric acid trihydrate (NAT) and ice particles are present. In 1988 the optical particle counter was modified by insulating the intake tube to keep aerosol near ambient temperature until measurement, by increasing the flow rate by a factor of 10, and by adding size discrimination at larger sizes (up to 5 μm radius on early units and 10 μm radius on later units), thus increasing the sensitivity to low concentrations of large particles. This counter was used successfully in Antarctica in 1988 [Hofmann, 1989; Hofmann and Deshler, 1989]. In 1989 the scattering angle of the high flow rate counter was increased from 27 to 40°. The effect of this change was to remove a double valued response in the region near 0.5 μm radius. This allowed us, for the first time, to resolve particles having radii between 0.3 and 1.0 μm.

In 1989 PSCs were observed in 4 out of 5 flights with this instrument at McMurdo Station, Antarctica [Hofmann and Deshler, 1990a]. This instrument was also successfully flown on 12 occasions in January and February 1990 in the Arctic at Esrange (68° N, 21° E) Kiruna, Sweden. PSCs were observed on 8 of these flights. A flight on 31 January followed a successful HNO_3 vapor flight by 23 hours [Schlager et al., 1990; Hofmann et al., 1990]. Combining these results indicated that HNO_3 depletion layers were caused by NAT condensation into clouds of very small particles in which growth had occurred on all the condensation nuclei, which were also measured. The average cloud particle radius was only 0.2 μm in contrast to the 3-5 μm observed for NAT particles in Antarctica [Hofmann and Deshler, 1990a]. This was due to the fact that the Arctic clouds were produced by recent fast cooling, which resulted in high vapor supersaturations [Hofmann et al., 1990], whereas the Antarctic clouds were the results of slow but persistent cooling and the concommittant depletion of most of the available HNO_3 vapor through condensation on relatively large ($r \geq 0.3$ μm) particles of the sulfate layer, producing a few large NAT particles [Hofmann et al., 1989; Hofmann and Deshler, 1990a]. This basic difference between Arctic and Antarctic PSCs, combined with the shorter period of a stable vortex, is the main reason why denitrification is not as common in the Arctic as in the Antarctic and thus a reason why ozone depletion is not as severe.

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The 6 February 1990 Event

On 6 February 1990, an unusual event occurred when the cold vortex rapidly intensified and temperatures reached values of -93° C over Kiruna, Sweden. Figure 1 shows temperature and ozone soundings near local noon on 4, 5, and 6 February and indicates a general cooling in the 18 to 24 km region on 4 and 5 February which was followed by a dramatic cooling event on 6 February. The tropopause moved up from about 9 to 10 to 12 km on the 3 days. The latter value is very unusual and suggests a major upward motion as the lapse rate between 10 and 12 km is nearly adiabatic. The temperature profiles indicated considerably more fine-scale structure before the 6 February event than after. Similar structure has been noted in temperature profiles obtained at McMurdo Station, Antarctica [Hofmann and Deshler, 1990a] and is believed to be related to air flow over nearby mountains.

In the 19 to 22 km region, the temperature profile again suggests cooling owing to upward motions. Temperatures reached -93.6° C at 21.5 km. Although water vapor was not measured, the results of Kelly et al. [1990], under similar conditions in January and February 1989 during the Airborne Arctic Stratospheric Expedition, indicated about 5 ± 0.5 ppmv water vapor at these altitudes. The temperatures observed at 21.5 km on 6 February were about 7° C below the frost point for 5 ppmv water vapor at that altitude and ice condensation should have occurred.

The 6 February sounding was followed by a particle counter - ozone flight about 6 hours later. The results are shown in Figure 2. The cold region had abated somewhat; however, a minimum of about -93° C was recorded near 22 km and a 3 km layer, from 20 to 23 km, was below the expected frost point. This region corresponded to a layer of very large particles, $r \geq 1$ μm, probably water ice clouds as suggested by the condensation temperatures. The ozone profile on both flights on 6 February indicated a large ozone reduction between 15 and 16 km. This feature was present to a lesser degree already on 5 February. Correlated reductions in the small particle concentrations in Figure 2 indicate that this feature is probably related to large-scale, quasi-horizontal transport as is common in the lower stratosphere.

The smooth curves in Figure 2 correspond to the background sulfate layer for size ranges $r \geq 0.15$ and 0.50 μm, determined earlier under warmer conditions. At about 15.5 km the temperature becomes cold enough to condense NAT for 5 ppmv water vapor and 10 ppbv HNO_3 vapor, the expected values in

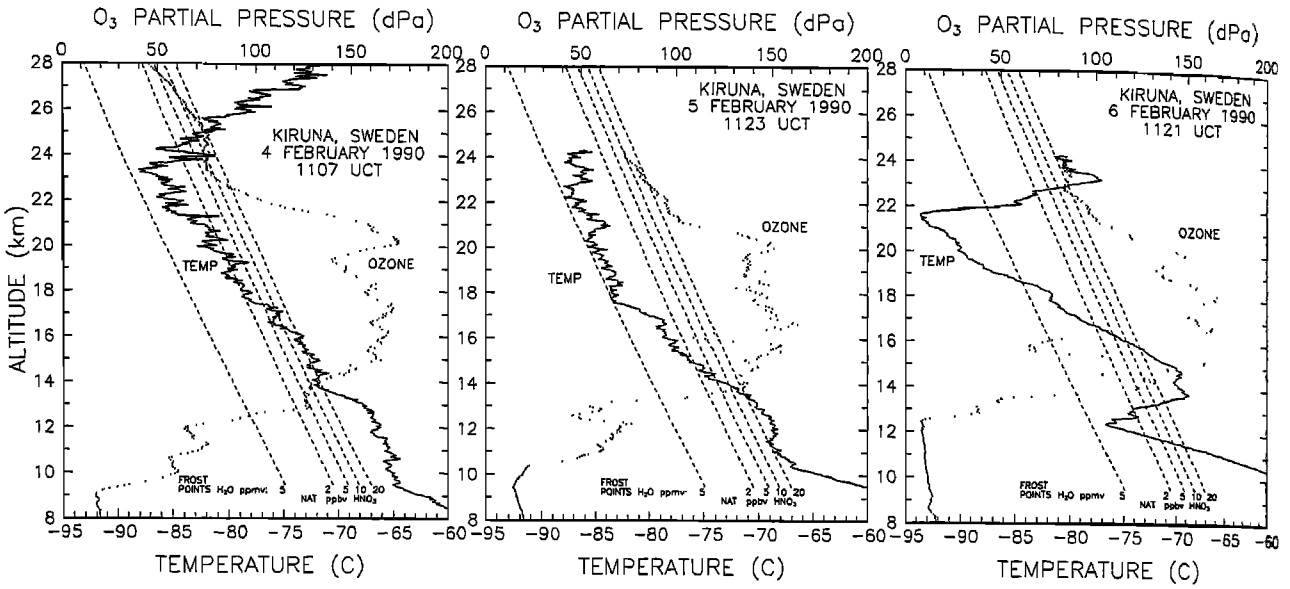

Fig. 1. Temperature and ozone profiles on 4, 5, and 6 February 1990 at Kiruna, Sweden. The dashed lines are condensation temperatures for water ice and nitric acid trihydrate for the indicated vapor mixing ratios.

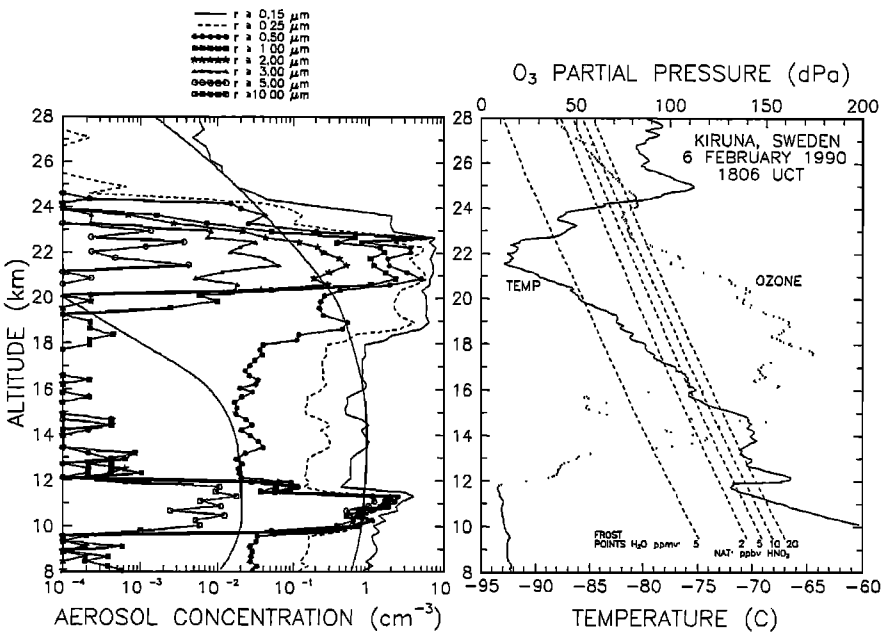

Fig. 2. Particle concentration profiles in 8 size ranges and temperature and ozone profiles on 6 February 1990 at Kiruna, Sweden. The smooth aerosol curves are sulfate aerosol profiles for radii greater than 0.15 and 0.50 μm as measured earlier under warmer conditions. The dashed temperature curves are condensation temperatures for water ice and nitric acid trihydrate for the indicated vapor mixing ratios.

the absence of substantial denitrification or dehydration. At this point, the $r \geq 0.50$ μm concentration begins to increase above the background level. When temperatures reach approximately the 1 ppbv HNO_3 vapor NAT condensation point (about 18 km), the smaller particles, $r \geq 0.15$ μm, also begin to increase above the background level and reach the concentration of condensation nuclei (CN), about 8 cm^{-3}, measured on 30 and 31 January and on 2 February. Thus, as concluded from the analysis of the 31 January flights [Hofmann et al., 1990], one interpretation of such data is that an HNO_3 vapor supersaturation of about 10 is required in order that NAT condensation occur on all available condensation sites.

An alternative explanation of the data in Figure 2 is that crystalline NAT forms at the expected temperature only on the larger particles of the sulfate layer, which may be frozen, and that the remaining smaller sulfate CN, which may be supercooled liquids, require lower temperatures for condensation of HNO_3 and water vapor into a supercooled liquid mixture. Hanson [1990] determined that such supercooled liquid mixtures form, but only about 1° C above the water frost point.

Thus, a supercooled liquid mixture of HNO_3 and H_2O in a weight ratio similar to NAT does not appear to explain the data since condensation occurs at temperatures warmer than 1° C above the frost point. Analysis of recent studies of the ternary mixture H_2SO_4-HNO_3-H_2O by Jaecker-Voirol et al. [1990] suggests that this system might exist at temperatures intermediate between the crystalline NAT condensation temperature and the water frost point [Hamill et al., 1990; D. Hanson, personal communication, 1990], i.e., several degrees above the water frost point which would correspond to the temperatures at which condensation on all of the CN was observed.

The small particle NAT distributions observed in Arctic PSCs typically contain HNO_3 mixing ratios of about 4 ppbv [Hofmann et al., 1990] or mass mixing ratios (including the water content) of about 16 ppb while the H_2SO_4-H_2O mass mixing ratio in the sulfate aerosol is only about 1-2 ppb in the current volcanically quiescent stratosphere. Thus, consideration of the ternary system cannot be important in the NAT particles observed. However, during the initial stages of condensation, the ternary system may be important and in that case would influence the interpretation of PSC onset temperature measurements. More research on the physical state of condensed nitric acid in PSCs and laboratory measurements of the condensation temperatures of the ternary state are required to carry these arguments any further.

The water ice cloud near the tropopause in Figure 2 was a common observation in the 1990 Kiruna data; however, the height of the tropopause on this occasion (12 km) was unusual. Concentrations of $r \geq 10\ \mu m$ particles reached values of about 0.01 cm^{-3} in the cloud. The bottom of the large particle layer occurred at 254 hPa with a temperature of -58.4° C while the top was at 184 hPa with a temperature of -71.7° C. For ice condensation to occur under these conditions, water vapor mixing ratios of 53 and 11 ppmv are required, respectively. The mass in the large particle mode, calculated from the size distribution assuming spherical water ice particles, is about 8 ppmv. Owing to the probable nonsphericity of the large ice particles, the uncertainty in this mass estimate is at least 50% and could be as large as a factor of 2. Comparing the water mixing ratio calculated from the cloud mass with that obtained from the condensation temperature suggests that only near the coldest region, at the top of the cloud, does the mass observed approach the value of that available for condensation.

Particle size distributions, determined from half-kilometer averages at several altitudes, are given in Figure 3. The derived differential lognormal distribution parameters and associated water or HNO_3 vapor mixing ratios, assuming either a water or NAT composition depending on temperature, as well as the reintegrated distribution, for comparison with the observations, are given. Shown are the size distributions at the lower edge (19.5 km), in the middle (21.5 km) and at the upper edge (23.5 km) of the cloud which was observed in the very cold region between 20 and 24 km. The ice saturation mixing ratios for average pressure and temperature values in these half-kilometer intervals are 6.0, 1.9, and 6.5 ppmv, respectively. If the actual water vapor mixing ratio in this region is 5 ± 0.5 ppmv, as observed in 1989, the observed cloud should contain water ice only at the cold center.

The size distribution at 19.5 km, at the base of the cloud where the temperature was -83.7° C, is unimodal with a modal radius of about 0.2 μm and an inferred HNO_3 condensed mass mixing ratio of 3.3 ppbv for NAT composition. These values are typical of NAT PSCs which have formed under rapid cooling (>5° C per day) in which condensation takes place on all available CN [Hofmann et al., 1990].

In the middle of the cloud at 21.5 km, a large particle mode is superimposed on a mode similar to that at 19.5 km. The large particle mode, with a modal radius of about 2 μm and a concentration of about 1 cm^{-3}, has too much mass to be composed of NAT and suggests the condensation of about 1.3 ppmv of water onto the preexisting NAT distribution. On the assumption that severe dehydration had not taken place in the 22 km region, these data suggest either an underestimation of the mass in the cloud by a factor of about 4, owing to the nonspherical particle shape, or that recent formation of the cloud, as air passed through the quasi-stationary, localized cold region, precluded the complete condensation of all the available

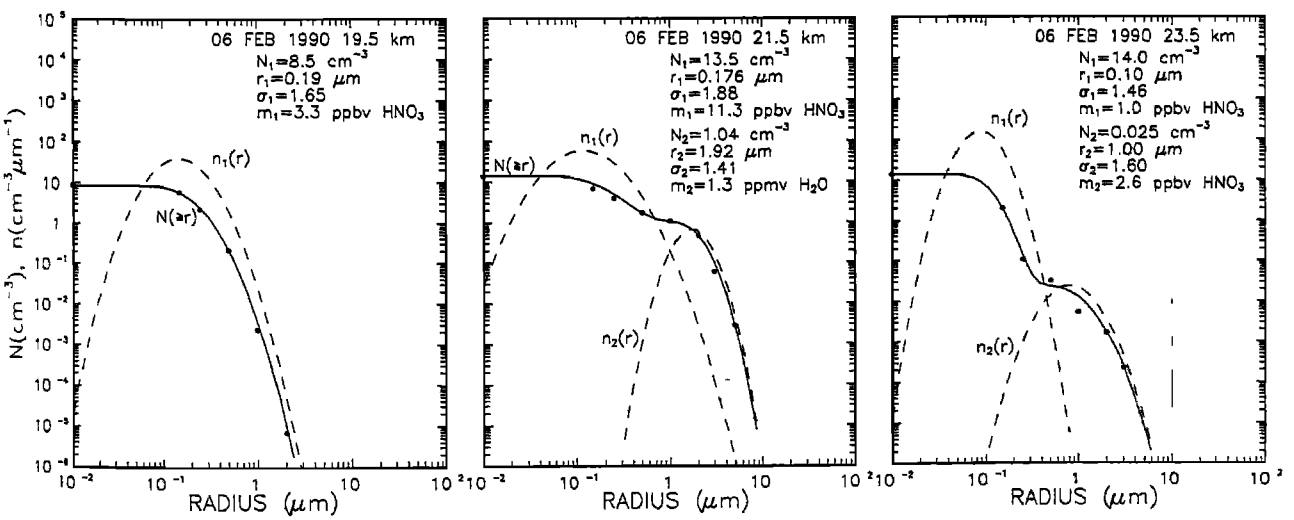

Fig. 3. Stratospheric cloud particle size distributions determined at 19.5, 21.5, and 23.5 km at Kiruna, Sweden on 6 February 1990. Points are measured integral concentrations. The dashed curves are derived differential lognormal distributions $n_i(r)$, having a total concentration of N_i, mode radius r_i, and distribution width σ_i. The full curves are the integral distributions, $N(\geq r)$ calculated from the $n_i(r)$. Mass mixing ratios given in the figure are calculated from the size distributions. The vertical lines in the 23.5 km graph indicate the statistical uncertainty for the 1/2 km averages used in obtaining the data points.

water vapor in the air parcel during the time available at temperatures below the ice point.

At the upper fringes of the cloud, at 23.5 km, the temperature has increased to -87.4° C, which is above the ice saturation point for 5 ppmv of water at this altitude. Although the size distribution is still bimodal, the composition of both modes is probably that of NAT inferring a combined mixing ratio of HNO_3 of about 3.6 ppbv, similar to the value at 19.5 km. Thus, in the very cold 19 to 23 km region, where one would expect the condensation of all available HNO_3, a substantial degree of denitrification (from about 10 ppbv to about 3.5 ppbv) may have occurred by 6 February.

The ozone minima between 22 and 24 km in Figures 1 and 2 were identified as being related to chemical ozone depletion in air which had an extended history at temperatures below -80° C [Hofmann and Deshler, 1990b]. Total ozone, as determined by integrating the partial pressure profile and assuming a constant mixing ratio above the highest altitude attained, was 341, 302 and 283 DU for the noon soundings on 4, 5, and 6 February, respectively, and 285 DU for the 1806 UCT sounding on 6 February. The two measurements of about 285 DU on 6 February, which are believed to be accurate to 5%, are in substantial disagreement with TOMS measurements of about 165 DU at this location on this day (A. Krueger, personal communication, 1990). A day earlier (5 February), TOMS indicated 200 DU while the ozonesonde measured 302 DU; however, before the ice cloud event, on 4 February, and after, on 7 February, the two techniques were in agreement to about 3%. This feature may be similar to ozone "miniholes" observed in the Antarctic spring, which are believed to be dynamic ozone perturbations of short duration [Newman et al., 1988]. In the case of the 6 February 1990 event over northern Scandinavia, the satellite observation appears to be an artifact caused by ultraviolet radiation backscattered from ice clouds present at 22 km on this day. Such radiation would not have penetrated as much ozone as radiation backscattered from tropospheric cloud tops, thus the apparently large ozone deficit. Either the cloud was not optically thick to ultraviolet radiation or the TOMS field of view of about 160 km square was larger than the cloud since only about 80 DU of ozone was present above the cloud.

Summary and Conclusions

Balloonborne measurements of ozone and particle size distributions at Kiruna, Sweden indicate that on 6 February 1990, a major cooling event occurred over northern Scandinavia, reaching temperatures as low as -93° C, in which both NAT and water ice clouds formed. The temperature of the appearance of the water ice clouds is consistent with about 5 ppmv of water vapor at 22 km. The particle size distributions suggest that a sizeable degree of denitrification had occurred in the 19 to 23 km region in this air mass. Although ozone levels appear to have been reduced by a small degree of chemical depletion, the ozone "minihole" of 165 DU observed by TOMS was probably an artifact since two ozonesonde measurements on that day indicated total ozone values of about 285 DU. It is suggested that backscattering of ultraviolet radiation from the ice cloud at 22 km caused an apparent large deficit in ozone in the TOMS measurements.

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